

REDUCTION OF HYDROUS FERRIC OXIDE TO A MAGNETIC
FORM WITH SODIUM DITHIONITE; IMPLICATIONS
FOR COAL MINE DRAINAGE TREATMENT

R. C. Streeter,¹ D. C. McLean, and H. L. Lovell

College of Earth and Mineral Sciences
The Pennsylvania State University
University Park, Pennsylvania

INTRODUCTION

The technique of neutralization with a cheap alkali, usually hydrated lime, is still the principal approach to coal mine drainage treatment today. As the number of these lime treatment plants has increased in response to stricter legislative controls, there has been a growing awareness that sludge dewatering and disposal present a major problem in the lime treatment process.

The sludge from a typical lime treatment plant is gelatinous and slow-settling; it rarely attains a solids content of more than five percent by weight after gravity settling; it cannot be dewatered economically with conventional mechanical dewatering equipment; depending on water quality and flow rate, the sludge can represent a significant percentage of the total throughput volume; and, the costs for sludge storage or disposal can increase operating expenses appreciably. Most of these problems could be alleviated if a method could be found to substantially increase the density of the sludge, either during or subsequent to the actual treatment process.

Various approaches to the control of mine drainage sludge properties have been reviewed by Lovell. (1) One such approach which has been the subject of a more extensive study (2), has involved the chemical reduction of the major sludge component, hydrous ferric oxide, to a ferromagnetic form.

Methods for the conversion of hydrous iron oxides in aqueous suspension to the magnetic ferrosferric oxide (magnetite) have been thoroughly documented in the chemical literature, although these processes are almost entirely concerned with either 1) partial oxidation of ferrous hydroxide, or 2) mixture of ferric and ferrous iron solutions in the proper stoichiometric amounts followed by the addition of alkali to precipitate the magnetic oxide. The third possible route, involving controlled partial reduction of hydrous ferric oxide, has received surprisingly little attention, possibly because the relatively strong reducing agents employed have tended to result in problems with reaction control (e.g. over-reduction of iron) as well as air-oxidation or decomposition of the reducing agent itself, leading to undesirable side reactions and reagent handling problems.

Unlike most of the reductants which reportedly yield a magnetic product on reaction with hydrous ferric oxide, sodium dithionite (sodium hydrosulfite)

¹ Present address: Bituminous Coal Research, Inc.
350 Hochberg Road
Monroeville, Pennsylvania 15146

is a commercially available, relatively inexpensive, and stable solid in dry air at room or slightly elevated temperatures. Its use in this application was first described in 1951 by Robl (3) and later mentioned by Ackermann (4), although neither of these authors reported in detail concerning the reaction stoichiometry, the effects of reaction variables such as temperature and pH, or the nature of the magnetic product. Consequently, the primary objective of this investigation was to conduct a more systematic study of the hydrous ferric oxide - sodium dithionite reaction, and to deduce whether this reaction might provide the basis for a feasible coal mine drainage treatment process. In line with this approach, the experiments were conceived to provide realistic analogies with coal mine drainage systems. For example, only sulfate salts of iron were used for the preparation of reagent solutions, and iron concentrations were maintained within representative limits.

A secondary objective of this research was to consider the effects of dissolved impurities on the reaction, since such effects are known to be of considerable significance. (5-8) Because the process envisioned involved the use of lime as an alkali, attention was focused largely on the effect of dissolved calcium.

EXPERIMENTAL

Most of the reactions were carried out using a 400-ml beaker containing 200 ml of reagent grade ferric sulfate solution. The beaker was fitted with a 1/8-inch thick Lucite cap containing four large holes to accommodate electrodes for pH and millivolt measurements. Three smaller holes were drilled in the cap through which a thermometer, nitrogen gas inlet tube, and buret (or reagent funnel) were introduced. The apparatus was mounted on a stirring hot plate, which provided temperature control to within $\pm 0.5^{\circ}\text{C}$ for experiments at elevated temperatures. Measurements of pH and electromotive force (Eh) during the reaction were accomplished using two Heath Model EUW-301 recording electrometers.

At the beginning of an experiment, stirring and nitrogen flow were commenced, and 1 N sodium hydroxide solution was added dropwise from a buret to achieve the desired pH (usually 10.0) in the system. The resulting suspension of hydrous ferric oxide was then purged continuously with nitrogen for a one-hour period to minimize decomposition of the dithionite by dissolved oxygen. The Eh of the suspension was monitored during this period, and usually reached a constant value within the last 30 minutes. Anhydrous sodium dithionite (Virginia Chemicals, Inc.; 94.3 percent purity) was then added to the deoxygenated suspension as a dry solid powder through a reagent funnel. It was found necessary to employ the dithionite in the solid form to avoid prior decomposition through hydrolysis or air oxidation.

The reaction was allowed to proceed for about six minutes, during which the pH was maintained at the desired level by further additions of 1 N sodium hydroxide. The suspension was then made up to constant volume with deionized water and aliquots were taken for iron analyses, sludge centrifugation and settling tests. Aliquots for iron analyses were filtered immediately with suction through a 30-ml fritted glass filter crucible, and filter cakes were dissolved in 2 ml of concentrated hydrochloric acid. Ferrous and total iron were determined by titration with 0.01 N potassium dichromate using sodium diphenylamine sulfonate as an internal indicator. Centrifugation tests were performed by centrifuging 15 ml aliquots of the suspension in graduated

centrifuge tubes at 3,100 rpm for 5 minutes. Settling tests were conducted using 100-ml graduated cylinders.

Magnetic properties of the reaction products were observed qualitatively with the aid of a small Alnico V horseshoe magnet.

In experiments involving the effect of dissolved calcium, weighed amounts of reagent grade calcium oxide were dissolved in the acidified ferric sulfate solution before alkalization with sodium hydroxide and subsequent addition of the dithionite. The Eh of the resulting suspension was monitored for a 1.5-hour period following dithionite addition.

RESULTS

The relationship found by these experiments between the mole percentage of Fe(III) reduced and the initial $\text{Fe(III):Na}_2\text{S}_2\text{O}_4$ molar ratio is shown in Figure 1. The equation of the best straight line through the experimental points was found to be

$$\log x = 2.3315 - 1.1760 \log y$$

where x = mole percentage of Fe(III) reduced

and y = $\text{Fe(III):Na}_2\text{S}_2\text{O}_4$ molar ratio.

If the experimental line is extrapolated, it is found that 100 percent reduction of Fe(III) occurs approximately at the point where the $\text{Fe(III):Na}_2\text{S}_2\text{O}_4$ molar ratio is equal to 2.0. Therefore, the theoretical reaction stoichiometry may be expressed more accurately by the relationship

$$\log x = 2.30103 - \log y$$

and this line is included in Figure 1 for comparison.

It should be noted that in the presence of excess dithionite, the reduction of hydrous ferric oxide continues beyond the point of reduction of one-third of the Fe(III) available (corresponding to the formation of magnetite). This was indicated by the appearance and magnetic properties of the reaction products. Thus, at high $\text{Fe(III):Na}_2\text{S}_2\text{O}_4$ molar ratios (excess Fe(III)) reaction products were more voluminous, only moderately magnetic, and brown in color, indicating the presence of unreacted Fe(OH)_3 ; at low $\text{Fe(III):Na}_2\text{S}_2\text{O}_4$ molar ratios (excess $\text{Na}_2\text{S}_2\text{O}_4$), reaction products were gelatinous, weakly magnetic, and blue-green in color, suggesting the presence of Fe(OH)_2 . Nevertheless, it is significant that ferromagnetic properties of the product were observed in varying degrees throughout the range $\text{Fe(III):Na}_2\text{S}_2\text{O}_4 = 3$ to 10.

The formation of the magnetic phase near an $\text{Fe(III):Na}_2\text{S}_2\text{O}_4$ molar ratio of 6 is further revealed by a plot of redox potential in the system versus the amount of dithionite added. This is shown in Figure 2, which indicates a break in the curve near the point corresponding to reduction of one-third of the Fe(III) present.

Distinct variations in the settling behavior of the product solids were observed with changes in the $\text{Fe(III)}:\text{Na}_2\text{S}_2\text{O}_4$ molar ratio. Curiously, optimum settling behavior and minimum solids volume, as measured by centrifugation tests, appeared to occur at an $\text{Fe(III)}:\text{Na}_2\text{S}_2\text{O}_4$ molar ratio near 6.5, corresponding to about 25 mole percent Fe(III) reduction for samples prepared at 30°C and pH 10. The results of experiments at other temperatures and pH values are summarized in Tables 1 and 2, respectively. All of the experiments indicated in Table 1 yielded magnetic products. On the other hand, changes in reaction pH at constant temperature (30°C) produced changes in the nature of the reaction product, as shown in Table 2.

TABLE 1. EFFECT OF TEMPERATURE ON THE REDUCTION OF HYDROUS FERRIC OXIDE BY SODIUM DITHIONITE AT pH 10^a

Temperature, °C	Mole Percent Fe(III) Reduced	Centrifugate Volume, ml	Percent Solids Vol. after 60 minutes ^b
10	22.66	0.50	13.7
20	20.65	0.45	12.5
30	21.65	0.48	12.7
40	21.94	0.52	14.1
50	22.53	0.60	17.8
60	21.71	0.65 ^c	18.9
70	21.92	0.52	18.9
80	19.73	0.44	9.8

^a $\text{Fe(III)}:\text{Na}_2\text{S}_2\text{O}_4$ molar ratio = 6.5 in all runs

^bGravity-settled solids

^cMechanical difficulties with the centrifuge were encountered; true centrifugate volume is probably less than 0.65 ml

The effect of pH on the reaction was also investigated in a series of tests at 80°C . In terms of the mole percentage of Fe(III) reduced, the results of these tests were essentially identical with those shown in Table 2. However, in all cases centrifugate volumes decreased markedly and settling rates were two to three times greater than those observed in the tests at 30°C . In addition, a phenomenon involving a color change of the solids from the orange-brown of amorphous Fe(OH)_3 to a distinct yellow-brown was observed to occur at 80°C during the one-hour nitrogen purge period

prior to the addition of dithionite. This color change appeared to be accompanied by a decrease in the gelatinous nature of the solids and the formation of more granular particles. In such cases, the reaction products were also more granular and showed a greater tendency toward flocculation in a magnetic field. Subsequent x-ray diffraction analyses revealed the presence of small amounts of crystalline α -FeOOH (synthetic goethite) in several of the reaction products prepared at 80°C.

TABLE 2. EFFECT OF pH ON THE REDUCTION OF HYDROUS FERRIC OXIDE BY SODIUM DITHIONITE AT 30°C^a

pH	Mole Percent Fe(III) Reduced	Centrifugate Volume, ml	Percent Solids Vol. after 60 minutes ^b	Nature of Reaction Product
8.0	26.08	1.50	72.5	dark olive-green, nonmagnetic
9.0	25.27	0.75	21.1	black, flocculent, moderately magnetic
10.0	21.65	0.48	12.7	black, strongly magnetic
11.0	19.41	0.66	18.0	black, strongly magnetic
12.0 ^c	0.37	1.38	43.0	orange, gelatinous, nonmagnetic

^aFe(III):Na₂S₂O₄ molar ratio = 6.5 in all runs

^bGravity-settled solids

^cpH electrode response was very sluggish near pH 12 and there is some question as to whether the desired pH was attained. Thus, the results of this run may be anomalous.

The effect of initial iron concentration was investigated briefly in a series of tests in which the reaction vessel was open to the air and no attempts were made to remove dissolved oxygen from the system. The results revealed that below an initial Fe(III) concentration of about 3×10^{-2} molar (ca. 1,700 mg/l) there was a gradual decrease in the apparent mole percentage of Fe(III) reduced.

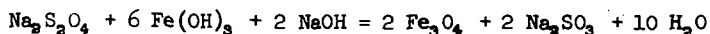
X-ray diffraction patterns of the freshly formed, magnetic reaction products corresponded to that of magnetite, and results of iron content analyses were very close to the theoretical value of 67.14 percent for $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$. On exposure to air, however, the initial reaction product was transformed to a rust-brown material with a corresponding decrease in iron content. This rust-brown material, which was still strongly ferromagnetic, was identified by x-ray diffraction analyses as $\gamma\text{-Fe}_2\text{O}_3$ (also hydrated).

The effect of calcium on the nature of the reaction product was investigated through a series of experiments in which increasing amounts of Ca^{2+} (as CaO) were introduced to the system before alkalization and reduction of the resulting solids by sodium dithionite. The Eh of the system was monitored throughout the course of the reaction, and usually reached a constant value within ± 10 millivolts about one hour after addition of the dithionite. There were no appreciable changes in the Eh, centrifugate volume, or appearance of the reaction product up to a Ca^{2+} concentration of about 1.2×10^{-2} molar. Above this concentration, however, the Eh of the system increased regularly and the reaction product became bulkier and less strongly magnetic. At a Ca^{2+} concentration of 2.4×10^{-2} molar, the reaction product was blue-green, gelatinous, and nonmagnetic, and appeared to consist largely of ferrous hydroxide. These results are summarized by Figure 3. Subsequent calculations showed that the point at which the observed changes began to occur in the system corresponded to the point at which the $(\text{Ca}^{2+})(\text{SO}_4^{2-})$ ion concentration product exceeded the solubility product of calcium sulfate dihydrate (gypsum) in the system (designated as K_{sp} in Figure 3). Also shown in Figure 3 are data from a similar study by Kakabadse et al. on the effects of Mg^{2+} . (8)

Several experiments were conducted using sludges prepared by alkalization (with NaOH , NH_4OH , or CaO) of actual coal mine drainage samples. In every instance, however, it was found impossible to effect a conversion of the sludge to a magnetic form by sodium dithionite reduction. On the other hand, if the iron was first oxidized (e.g. by H_2O_2), fractionally precipitated as $\text{Fe}(\text{OH})_3$ below pH 4, and separated from the liquid phase, conversion of the sludge to a magnetic form was readily effected and the results were essentially the same as those obtained using pure iron solutions. For those experiments where lime was used as the alkali, however, it was necessary to heat the suspension to at least 80°C to effect the desired conversion.

DISCUSSION

The experimental data indicate that the reduction process can be represented by the following overall reaction:



This reaction is similar to one proposed by Ackermann based on theoretical considerations. (4) It should be emphasized that no attempts were made in this study to isolate or identify the sulfur-containing by-product(s) of the reaction. The aqueous chemistry of dithionites is quite complex, and their oxidation can result in several species depending on reaction conditions. (9) Moreover, side reactions due to hydrolysis (10) or thermal decomposition (11) are common. In fact, loss of dithionite through such side reactions is believed to account in part for the discrepancies encountered in these studies between the theoretical and empirical stoichiometries, as reflected by Figure 1. A second factor which undoubtedly affected the results involved the oxidation of the reaction product to hydrated γ - Fe_2O_3 . The available evidence indicated that this oxidation was sufficiently rapid during the first few minutes following preparation of the magnetic product to result in significant negative errors in the analytical determinations of Fe(II) .

As mentioned earlier, reaction products exhibiting the maximum densities and fastest settling rates were found by experiment to have an $\text{Fe(III)}:\text{Fe(II)}$ molar ratio of about 3, corresponding to 25 percent Fe(III) reduction. Since both extraneous losses of dithionite and negative errors in the Fe(II) determination would have the effect of increasing the apparent $\text{Fe(III)}:\text{Fe(II)}$ ratio, it is possible that such reaction products did in fact correspond closely to true hydrated magnetites ($\text{Fe(III)}:\text{Fe(II)} = 2.0$) at the actual time of preparation. However, it is interesting that Hoak and Sindlinger, during their development of a process for the recovery of ferrosulfuric oxide from steel plant waste pickle liquors, observed that optimum settling rates were obtained when the $\text{Fe(III)}:\text{Fe(II)}$ molar ratio of the product was in the range of 2.5 to 3.5 (average 3.0). (12)

Variations in reaction temperature throughout the range 10 to 80°C appeared to have little effect on the reaction stoichiometry (Table 1). To the contrary, increases in the reaction pH throughout the range 8 to 12 resulted in definite decreases in the amounts of Fe(III) reduced (Table 2). This phenomenon is believed to be associated with the depressed dissociation of Fe(OH)_3 with increasing pH, together with the supposition that the dithionite reduction proceeds through a solution mechanism involving the ferric ion. (4) It is apparent that, under the experimental conditions employed, optimum properties of the reaction product with respect to solids volume, settling rate, and magnetic response occurred at pH 10.

The results of experiments on the effect of initial iron concentration indicated that the role of dissolved oxygen in the system (i.e., through consumption of dithionite) became apparent below an Fe(III) concentration of about 3×10^{-3} molar. At an experimental $\text{Fe(III)}:\text{Na}_2\text{S}_2\text{O}_4$ molar ratio of 6, the sodium dithionite concentration corresponding to this apparent limit would be about 5×10^{-3} molar, and this value is in agreement with that reported by Conley et al. in studies on the dithionite reduction of Fe^{3+} in neutral or acidic media. (13) In terms of practical application of the reaction, these results suggest that the initial Fe(III) concentration should be much greater than that of dissolved oxygen in order to prevent the latter from exerting a significant influence on the overall reaction stoichiometry.

There were indications throughout this investigation that factors affecting crystal growth are of considerable importance in the formation

and stability of the magnetic reaction product. Thus, the most strongly magnetic, densest, and fastest settling products were prepared under conditions which enhance crystal ordering, such as elevated reaction temperatures and the absence of impurities. The effect of temperature was especially apparent at or above 80°C, and x-ray data indicated that the improved properties of the reaction product may have been largely due to the conversion of amorphous $\text{Fe}(\text{OH})_3$ to crystalline $\alpha\text{-FeOOH}$ at these elevated temperatures, prior to the reaction with $\text{Na}_2\text{S}_2\text{O}_4$.

With regard to the effects of impurities in the system, it has been well established that the presence of foreign species in solution or suspension ordinarily has an adverse effect on ordering during crystal growth. (14, 15) A case in point involves the apparent adverse effects of coprecipitated gypsum on the magnetic and other properties of the reaction products prepared by dithionite reduction of $\text{Fe}(\text{OH})_3$. Of further relevance, it has been reported that interfering effects of other species (e.g. aluminum, magnesium) on the formation of magnetite in aqueous suspension are significant only within the pH ranges where these elements exist in the form of insoluble hydroxides or hydrous oxides. (6) Thus, it is quite conceivable that the mode of interference may be similar in all cases. Although some workers have implied that the mode of interference may involve cation substitution or colattice formation in the magnetic phase, the only compelling evidence for this type of mechanism has been that given by Kakabadse et al. for the case of magnesium inhibition, and even in this instance the magnesium was evidently present in the system as magnesium hydroxide. (8)

The results of Kakabadse et al. on the effects of magnesium are shown in Figure 3 for comparison. The first maximum in the redox potential curve corresponds to the consummated formation of a "magnesio-wustite" ($\text{MgO}\cdot\text{FeO}$) sublattice within the inverted spinel lattice of magnetite. This maximum was always found to occur at a $\text{Mg}^{2+}:\text{Fe}^{2+}$ molar ratio of 1.0. At higher $\text{Mg}^{2+}:\text{Fe}^{2+}$ ratios, ferrous iron was presumably replaced by Mg^{2+} with concurrent loss of magnetic properties of the precipitate, until complete substitution occurred (indicated by the second redox potential maximum). The overall process was marked by significant increases in the volume of centrifugate solids, as shown by Figure 3.

Despite certain dissimilarities in the procedures employed by these workers compared with those of the present study, the results shown by Figure 3 on the effect of calcium reveal that there were no sudden changes or significant reversals in the Eh of the system which could be correlated with some integer $\text{Ca}^{2+}:\text{Fe}^{2+}$ molar ratio. Thus, there is no evidence from the present study to indicate that the mechanism of calcium interference involves substitution by Ca^{2+} for Fe^{2+} in the magnetite crystal lattice.

In view of the findings during this investigation, it seems apparent that a conceptual coal mine drainage treatment process involving the sodium dithionite reduction of hydrous ferric oxide would require some rather significant departures from the simple mixing-aeration-settling operations common in current practice. This is exemplified by the flowsheet shown as Figure 4. The conceptual process indicated by Figure 4 includes the following major steps:

1. Oxidation and fractional precipitation of iron at $\text{pH} \leq 4$. This approach is necessary to minimize the residual dissolved iron concentration

as well as to prevent interferences due to coprecipitated aluminum hydroxide. (6, 16) Since the rate of ferrous iron oxidation with gaseous oxygen is impractically slow under these conditions, the use of catalysts or strong chemical oxidants such as hydrogen peroxide or ozone would appear to be necessary.

2. Sludge concentration and separation. Thickening of the precipitated hydrous ferric oxide and its separation from the bulk of the process flow would be necessary to reduce that volume of material requiring subsequent thermal and chemical treatment, as well as to reduce interference by dissolved oxygen.

3. Alkalization of the concentrated sludge to near pH 10 and heating of the sludge suspension to at least 80°C. The data show that optimum properties of the reaction product are obtained under these conditions. In addition, the heating step presupposes the use of lime as an alkali in the process, and is dictated by the need to overcome possible interference due to coprecipitated gypsum.

4. Addition of solid sodium dithionite to the heated, alkaline suspension. In actual practice, an amount of $\text{Na}_2\text{S}_2\text{O}_4$ in slight excess of that required by the stoichiometric ratio $\text{Fe(III)}:\text{Na}_2\text{S}_2\text{O}_4 = 6.0$ would probably be necessary to compensate for losses due to hydrolysis, air oxidation, or thermal decomposition during reaction with the heated sludge.

5. Magnetic sludge recovery. This could conceivably involve thickening and/or magnetic separation techniques, using wet drum separators of the type employed in heavy media recovery operations.

The potential advantages of the process outlined above would be the elimination of aeration facilities, holding lagoons, and sludge settling basins, as well as the possibility of higher treatment capacities and the recovery of saleable products.

On the other hand, economic considerations reveal that reagent costs would probably be excessive. For example, treatment of a coal mine water containing 800 mg/l of iron by the dithionite reduction process would involve a cost for sodium dithionite alone of nearly \$1.00 per 1,000 gallons of water treated. In pilot plant tests, a coal mine water of similar composition was treated by conventional lime neutralization at a total (capital and operating) cost varying between \$1.09 and \$1.28 per 1,000 gallons. (17)

In summary, it is doubtful whether the dithionite reduction process would be economically feasible by present-day standards, since the relatively complex flowsheet (Figure 4) indicates the likelihood of a larger capital investment and increased operating costs for chemical reagents and sludge heating. Further developmental work should be undertaken, however, before a final judgement is made.

Acknowledgments

This research was supported by funds from the Mineral Conservation Section of the College of Earth and Mineral Sciences, The Pennsylvania State University.

REFERENCES

1. Lovell, H. L., "The control and properties of sludge produced from the treatment of coal mine drainage water by neutralization processes," 3rd Symp. Coal Mine Drainage Res. Preprints, Pittsburgh, Pa., by Coal Ind. Advisory Comm. to Ohio River Valley Water Sanit. Comm., 1970. pp. 1-11.
2. Streeter, R. C., "Reduction of hydrous ferric oxide to a magnetic form with sodium dithionite; implications for coal mine drainage treatment," Ph.D. Thesis, The Pennsylvania State University, 1971.
3. Robl, R., "Magnetizable ferric oxides," Ger. Patent 801,723, 1951; Chem. Abstr. 45, P4009b (1951).
4. Ackermann, G., "Magnetic recording media. V. Reduction of iron(III) hydroxide with formamidinesulfinic acid," J. prakt. Chem. 5 (4), 298-309 (1958).
5. Kakabadse, G. J. and P. Whinfrey, "Sodium silicate - ferrous hydroxide system," Nature 189, 829 (1961).
6. Kakabadse, G. J. and P. Whinfrey, "The effect of certain ions on the formation of magnetite from aqueous solution," Ind. Chim. Belge 29 (2), 109-12 (1964).
7. Riddoch, J., "The hydrolytic and redox properties of ferric iron, with special reference to the effect of magnesium ions above pH 10," Ph.D. Thesis, Victoria University, Manchester, England, 1964.
8. Kakabadse, G. J., J. Riddoch, and D. St. P. Bunbury, "The effect of magnesia on the formation of magnetite from aqueous solution," J. Chem. Soc. (A), 1967, 576-9.
9. Rinker, R. G., T. P. Gordon, D. M. Mason, R. R. Sakaida, and W. H. Corcoran, "Kinetics and mechanism of the air oxidation of the dithionite ion ($S_2O_4^{2-}$) in aqueous solution," J. Phys. Chem. 64, 573-81 (1960).
10. Spencer, M. S., "Chemistry of sodium dithionite," Trans. Farad. Soc. 63 (10), 2510-15 (1967).
11. Rinker, R. G., S. Lynn, D. M. Mason, and W. H. Corcoran, "Kinetics and mechanism of the thermal decomposition of sodium dithionite in aqueous solution," Ind. Eng. Chem., Fundamentals 4 (3), 282-8 (1965).
12. Hoak, R. D. and C. J. Sindlinger, "New technique for waste pickle liquor neutralization," Ind. Eng. Chem. 41, 65-70 (1949).
13. Conley, R. F., H. J. Golding, and M. W. Taranto, "Improvement of iron bleaching in clays through potentiometric control of sodium dithionite addition," Ind. & Eng. Chem., Process Des. Develop. 3 (4), 183-8 (1964).
14. Buckley, H. E., "Crystal Growth," John Wiley & Sons, Inc., New York, N. Y., 1951. Chapter 10, "Crystal habit modification by impurities."

15. Harbury, L., "Solubility and melting point as functions of particle size. II. The induction period of crystallization," J. Phys. Chem. 51, 382-91 (1947).
16. Stauffer, T. E. and H. L. Lovell, "The oxygenation of iron(II) - relationship to coal mine drainage treatment," Special Research Report SR-69 to the Pennsylvania Coal Research Board, The Pennsylvania State University, 1968.
17. "Operation Yellowboy," report submitted to the Pennsylvania Coal Research Board by Dorr-Oliver, Inc., Stamford, Connecticut, June, 1966.

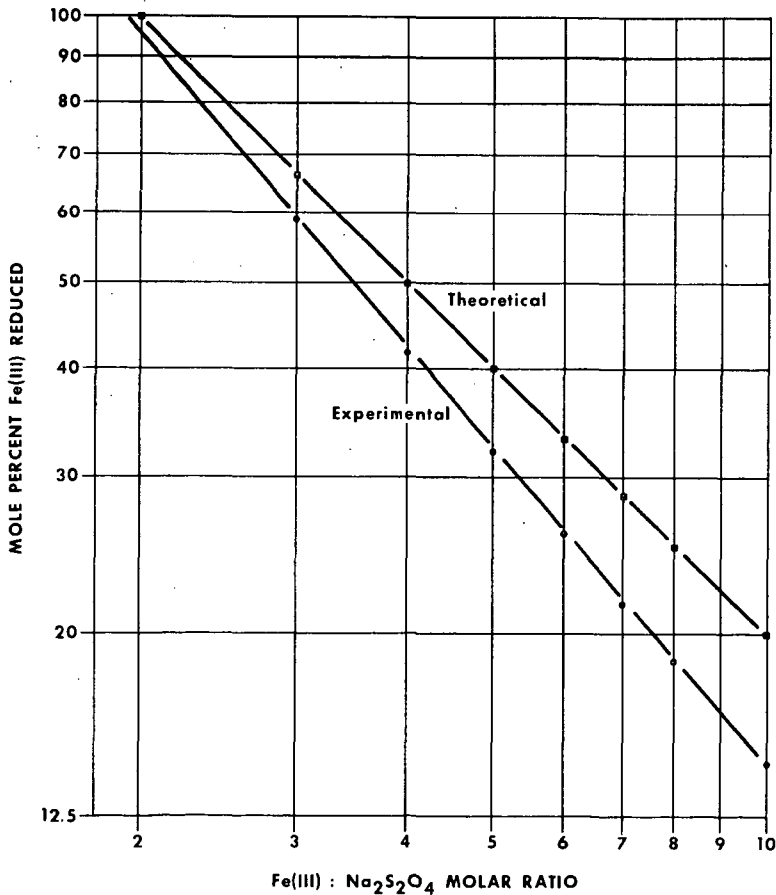


Figure 1. Mole Percent Iron (III) Reduced as a Function of Fe(III):Na₂S₂O₄ Molar Ratio at pH 10 and 30°C

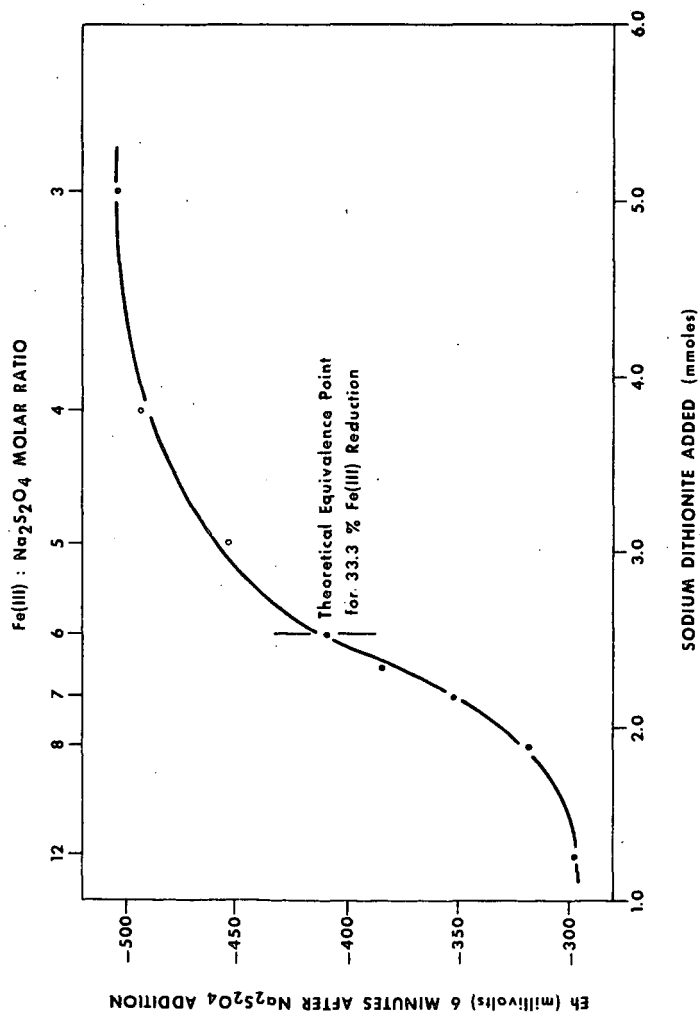


Figure 2. Change in Redox Potential During the Reduction of 15.19 mmoles of Hydrous Ferric Oxide at pH 10 and 30°C with Increasing Amounts of Sodium Dithionite

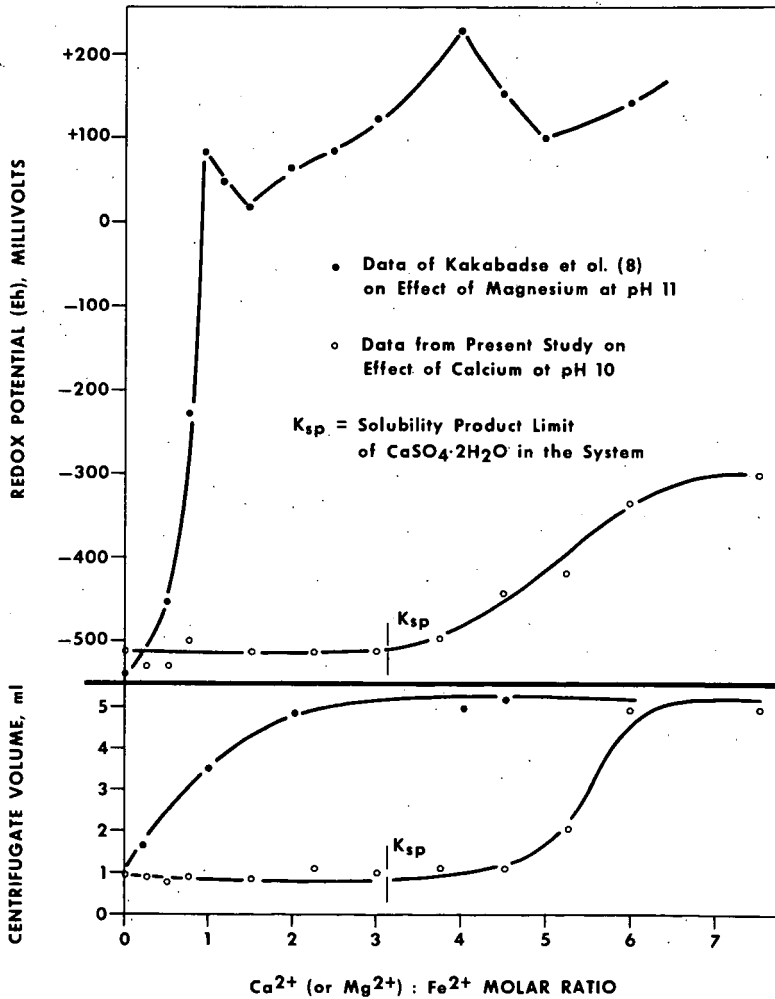


Figure 3. Variation of Redox Potential and Centrifugate Volume with Increasing Ca^{2+} (or Mg^{2+}): Fe^{2+} Molar Ratio

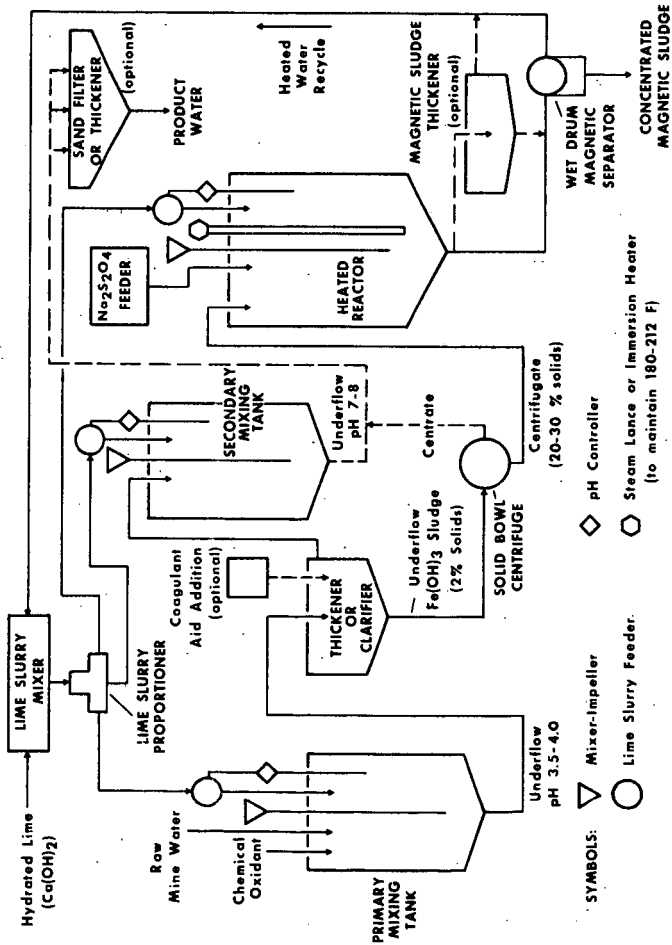


Figure 4. Conceptual Design of Coal Mine Drainage Treatment Process for the Recovery of Magnetic Sludge by Sodium Dithionite Reduction of Fractionally Precipitated Ferric Oxide